DRAFT TECHNICAL REVIEW AND EVALUATION
OF APPLICATION FOR
AIR QUALITY PERMIT NO. 31094

I. INTRODUCTION

This Class II, synthetic minor source air quality control operating permit is for the operation of a chemical synthesis and repackaging facility near Kingman in Mohave County, Arizona. The facility is owned and operated by Praxair, Inc.

Company Information

Facility Name:	Praxair, Inc.
Facility Location:	Lat 35 1 40, Long 114 8 36
Mailing Address:	PO Box 6157 Kingman, Arizona, 86402

Background

This source is a chemical synthesis and repackaging facility, located near Kingman, Arizona. This facility has been operating since 1990. This facility manufactures arsine and phosphine, and fills and warehouses gaseous products used by the semiconductor industry. These gaseous products include diethyltelluride, silane, diborane, dichlorosilane, trichlorosilane, ammonia, hexafluoroethane, octafluorocyclobutane, octafluorotetrahydrofuran, perfluoropropane, tetrafluoromethane, trifluoromethane, sulfur hexafluoride, argon, helium, hydrogen and nitrogen.

II. PROCESS DESCRIPTION

A. Arsine Synthesis

Arsine is synthesized by the reaction of mixing zinc arsenide with sulfuric acid to produce zinc sulfate and pure arsine gas. The synthesis reaction takes place in isolated rooms using a process that is totally remote-controlled. The production systems have vent lines that exhaust to the Arsine Guardian combustion units, through Arsine Baghouses for particulate matter removal, and then to the Ventilation Emergency Scrubber (VES). The synthesis rooms have ventilation systems that exhaust the entire air contents of the rooms to the VES.

B. Phosphine Production

Phosphine is synthesized by the pyrolytic (adding heat) reaction of phosphorous acid to produce phosphoric acid and pure phosphine gas. The synthesis reaction takes place in isolated rooms using a process that is totally remote-controlled. The production systems have vent lines that exhaust to the Phosphine Guardian combustion unit, through the Dynawave Scrubber system, and then to the VES. The synthesis rooms have ventilation systems that exhaust the entire air contents of the rooms to the VES.

C. Cylinder processing and filling

The Permittee fills and processes cylinders for arsine, phosphine, diethyltelluride, silane, diborane, dichlorosilane, trichlorosilane, ammonia, hexafluoroethane, octafluorocyclobutane, octafluorotetrahydrofuran, perfluoropropane, tetrafluoromethane, trifluoromethane, and sulfur hexafluoride. Cylinders are purged of residual product and evacuated, then inspected and reconditioned as necessary (including shot blasting and painting) before refilling. Residual product (excluding ammonia, hexafluoroethane, octafluorocyclobutane, octafluorotetrahydrofuran, perfluoropropane, tetrafluoromethane, trifluoromethane and sulfur

hexafluoride) is exhausted to a primary disposal system first (Guardian combustion unit, wet scrubber, etc.) and then to the VES.

III. EMISSIONS

Praxair's installation permit contained an hourly arsine emissions limit of 0.222 g/hr. This limit was based on Arizona Department of Health guidance issued in 1989. In 1992, the Arizona Ambient Air Quality Guidelines (AAAQGs) were revised. The 1992 AAAQGs include hourly, 24-hour and annual thresholds. These are health based thresholds that ensure protection of public health and the environment. The Department is allowing Praxair to adjust their arsine emissions limit based on these thresholds, and the facility conducted an ambient air impact analysis (see Section VIII of this document) to demonstrate that they would not be exceeded. The revised limits are 2.58 g/hr, with a maximum of 110.25 grams in any rolling 24-hour period and 779.76 grams in any rolling 365-day period. The revised emission limits in the permit are based on the AAAQG thresholds for arsine.

Table 1, below, lists the potential emissions from the control devices at the facility.

Table 1: Controlled Potential to Emit

Equipment	Pollutant	Controlled PTE (ton/year)
VES	Arsine	0.025
VES	Phosphine	0.000194
VES	Diborane	0.0000025
VES	Silane	0.000475
Ammonia Scrubber	Ammonia	0.144

A. The cylinder shot blasting operation has the potential to emit 0.09 tpy of particulate matter.

B. Emissions of criteria pollutants are produced from the Emergency Generator, the Fire Water Pump Engine and the Diesel Scrubber Pump. These engines are limited to 2,000 hours of operation per year. Under this restriction, the engines have the potential to emit 5.97 tpy of CO and 27.71 tpy of NO_X.

IV. APPLICABLE REGULATIONS

The applicable regulations were identified by the agency as part of the application packet. If necessary, the source is required to list any additional regulations that may be applicable. Table 2 displays the applicable requirements for each piece of equipment under this proposed permit.

Table 2: Verification of Applicable Regulations

Unit	Date of Constr./Mod.	Control Device	Rule	Verification
Synthesis and Handling Operations	N/A	Baghouses, combustion units and scrubbers	AAC R18-2-702 and -730	PM and odor limits for Unclassified Sources, and general opacity limits.
Shot Blasting	N/A	Dust Collector	AAC R18-2-726	This standard applies to the cylinder shot blasting activities
Spray Painting	N/A	Paint booth filters	AAC R18-2-727	This standard applies to cylinder spray painting activities
Internal Combustion Engines	N/A	N/A	AAC R18-2-719	This standard applies to all stationary rotating machinery

Fugitive dust sources	N/A	Water and other reasonable precautions.	AAC R18, Article 6	These standards are applicable to all fugitive dust sources.
Mobile sources	N/A	Water Sprays/Water Truck for dust control	AAC R18, Article 8	Opacity requirements for smoke and dust for mobile sources (construction equipment, etc.).

V. MONITORING AND RECORDKEEPING REQUIREMENTS

A. VOC, HAPs and Gaseous Emissions

1. To ADEQ's knowledge, there is no CEMS technology currently available with the capability to directly measure arsine emissions at the levels that this facility emits. Therefore, the Permittee has proposed a program of parametric monitoring to demonstrate compliance with the emission limits in the permit. The parameters to be monitored include, among others, the combustion unit temperatures, scrubber air and liquid flow rates, and scrubber solution concentrations. Specific parameters are outlined in the Parametric Monitoring Plan, contained in the permit as Attachment "C". Minimum temperatures for the combustion units and maximum air flow rate and minimum $KMnO_4$ flow rate for the Ventilation Emergency Scrubber are derived from the results of a stack test conducted in November, 2005. Other parameters are taken from manufacturer recommendations. The Permittee is required to monitor and record the parameters, and to report any deviations from these parameters to ADEQ pursuant to the excess emission reporting requirements in Section XII of Attachment "A.".

2. The Permittee is required to keep records of the facility's hours of operation and arsine production, and to conduct a performance test for arsine emissions annually. The results from the most recent stack test are to be used, along with the hours of operation and arsine production, to calculate the hourly, 24-hour and annual emissions, as applicable, to show compliance with the emission limits in the permit.

3. The Permittee is also required to continuously monitor for total hydrides at the fencelines. The facility uses a Vertex system that monitors hydride concentrations at various points, both inside the buildings and outside the facility, at the process area boundary. Alarms and automatic shutdowns occur at predetermined concentrations, depending on the location. Alarms from the fenceline monitors or the VES stack monitor are to be reported to ADEQ.

B. Opacity Requirements

The permit specifies opacity limitations for the various emission sources found within the facility. The permit requires the source to perform monthly observations of the various point source and fugitive dust emissions plumes, and if a plume appears to exceed the opacity standard, a Method 9 observation is to be conducted.

The Permittee is to keep records of the date, time, and results of any Method 9 observation made, as well as the name of the observer who conducted the test.

C. Particulate Matter Requirements

The permit specifies particulate matter limits for the internal combustion engines and fugitive dust sources. The Permittee is required to keep records of all activities that may produce fugitive dust emissions of particulate matter, and to keep records of the control measures employed to reduce fugitive dust.

VI. COMPLIANCE HISTORY

The facility has been recently inspected five times with two inspections resulting in the below described Notices of Violation (NOVs).

A. In 2004, as a result of a series of inspections, ADEQ issued a Notice of Violation to Praxair, Inc. The NOV, Case Number 31355, alleged three permit violations, and two violations of the Arizona Administrative Code, as described below. On December 20, 2005, Praxair, Inc. paid a penalty of $550,000 to ADEQ and entered into a Consent Judgment to settle the outstanding enforcement issues identified in the NOV. The Consent Judgment currently remains open. The counts of the NOV included the following:

1. Non-compliance with **Permit Number 65024 (LTF No. 24698) Condition V.B. –** ***The Permittee shall submit a plan for OAQ approval to continuously monitor and record the total volumetric flowrate of gases vented from the tail gas stack and to monitor and record the concentrations of arsine, phosphine, silane, dichlorosilane, and diborane at the exit of the "Guardian" environmental scrubber. Based on the above measurements, Permittee shall calculate at the end of each clock hour, the average emission rate (in grams per hour) of each of the above gases.*** The citation factual description explained that ADEQ's review of data produced by Praxair, Inc. from the MDA 16 and Vertex monitoring systems for 2003, revealed failure to continuously monitor and record concentrations of hydride gases and dichlorosilane, as required by the Permit, and as committed to under the April 27, 1990, Ambient Air Monitoring Program, and the July 3, 1990, Process Area and Stack Monitoring Program (the "plan"). Also, total volumetric flow rate was monitored but not continuously recorded; and no calculations of the average emission rates of hydride and dichlorosilane gases were made at the end of each clock hour.

2. Non-compliance with **Permit Number 65024 (LTF No. 24698) Section V.C. – For** ***each scrubber system, a gauge shall be installed to indicate, in inches of water, the static pressure differential and the scrubber liquid recirculation rate.*** The citation factual description explained that Praxair, Inc. failed to install an operational gauge that measured the scrubber liquid recirculation rate between July 7, 2003, and January 28, 2004. During ADEQ's inspection on January 6, 2004, ADEQ found the scrubber liquid recirculation rate gauge to be inoperable. A subsequent review of the VES Scrubber Control Log Book found the scrubber liquid recirculation rate gauge was inoperative between July 7, 2003, and January 28, 2004.

3. Non-compliance with **Permit Number 65024 (LTF No. 24698) Section III.B. –** ***Within 180 days of issuance of this Permit, Permittee shall begin the sampling and analysis of ambient particulate matter using a PM-10 Reference or Equivalent Method. Location of this monitor shall be approved in advance by the OAQ. Sampling time and frequency shall correspond with the national particulate sampling schedule.*** The citation factual description explained that during 2003, Praxair, Inc. failed to sample and analyze ambient particulate matter according to the sampling time and frequency corresponding with the national particulate sampling schedule during calendar year 2003, as required by the Permit, and as committed to in the April 27, 1990, Amended Ambient Air Monitoring Program. During the first quarter of 2003, ambient sampling was performed on 10 dates and none of these sample sets were obtained on the 15 required sampling days. During the second quarter of 2003, ambient sampling was performed on 12 dates and only 4 of these sample sets were obtained on the 15 required sample days. During the third quarter of 2003, ambient sampling was performed on 8 dates and only 1 set of samples was obtained during the 16 required

sample days. No sampling was performed during the fourth quarter of 2003, during which sampling was required on 15 sample days.

4. Non-compliance with **A.A.C. R18-2-302.B.1.a – *Construction or operation of a major source without a Class I permit.*** The citation factual description explained that Praxair, Inc. has operated a major source without first obtaining a Class I permit. ADEQ's calculations showed the potential to emit (PTE) of the hazardous air pollutant arsine at 22.8 tons/yr. before controls from 3 synthesis reactors on November 15, 1993, the effective date of adoption and incorporation of Title V of the 1990 amendments to the Clean Air Act. ADEQ determined the calculation of PTE before controls of arsine was appropriate since Installation Permit No. 65024 does not contain limitations and conditions which are "federally enforceable" or "enforceable as a practical matter" as these terms are defined respectively in A.A.C. R18-2-101.45 and A.A.C. R18-2-306.01.A. Based upon Praxair, Inc.'s admitted inability to measure individual hydride gas emissions down to the levels required in the Installation Permit, and the lack of specific permit requirements for the operation of the VES scrubber, there were no practicably enforceable limits in Permit #65024 (LTF #24698) for the individual hydride gases.

5. Non-compliance with **A.A.C. R18-2-303.B.14 – *Failure to submit a permit application on or before May 1, 1995 for a source requiring a Class I permit that was in existence on November 15, 1993.*** The citation factual description explained that Praxair, Inc. failed to submit an application to renew Installation Permit No. 65024 as a Class I permit on or before May 1, 1995, as required, for "other sources requiring Class I permits."

B. On August 9, 2006, ADEQ issued an NOV to Praxair, Inc. The NOV, Case Number 73031, alleged one permit violation, as described below. This NOV currently remains open. The count of the NOV is as follows:

Non-compliance with **Minor Permit Revision Number 1001644, Section VII.A of Attachment "A" – *Failure to submit a compliance certification to the Director annually by January 31st for the previous calendar year.*** The citation factual description explained that Praxair, Inc. failed to submit the annual compliance certification for the period from January 1, 2005, to December 31, 2005. This certification report was due on January 31, 2006.

C. On January 5, 2007, ADEQ issued an NOV to Praxair, Inc. The NOV, Case Number 76623, alleged four permit violations, as described below. This NOV currently remains open. The counts of the NOV are as follows:

1. Non-compliance with **Permit No. 23262**, **Attachment "A," Condition II-Emission Limits – *Permittee shall not emit in excess of 0.222 grams/hour of arsenic compounds, including arsenic, arsine, arsenic trioxide, and arsenic pentoxide.*** The citation factual description explained that on October 22, 2006, Praxair reported excessive emissions of 37.1 grams/hour of Arsine for the hour ending at 10:00 am and 4.07 grams/hour of arsine for the hour ending at 11:00am. The excessive emissions represent 18 to 165 times the current permit limit. The compliance conditions for the above violation included providing a management plan for the violations that describes the short-term and long-term preventative measures and actions taken to remedy the excessive emissions at the facility and to ensure that the events do not reoccur. The facility's deadline to achieve compliance was on January 24, 2007, and February 16, 2007, which was achieved on January 24, 2007, and January 31, 2007.

2. Non-compliance with **Permit No. 23262**, **Attachment "A," Condition II-Emission Limits –** ***Permittee shall not emit in excess of the following compounds: arsenic Compounds, including arsine (0.222 grams/hour), phosphine (0.093 grams/hour), diborane (0.068 grams/hour), dichlorosilane (42.24 grams/hour), silane (2.807), and diethyltelluride (0.0002 grams/hour).*** The citation factual description explained that excessive emissions were reported to ADEQ by Praxair on 2/22/06, 3/15-16/06, 5/15/06, 6/24/06, 8/7/06, 8/16/06, 9/13/06, 9/19/06, 9/26/06, 10/4/06, and 10/19/06. The excessive emissions included arsine and diborane releases. The associated releases at the Praxair facility were approximately 6 to 45 times the permit limitations. The facility's deadline to achieve compliance was on January 24, 2007, and February 16, 2007, which was achieved on January 24, 2007, and January 31, 2007.

3. Non-compliance with **Civil Judgment CV2005-018397, Section VII.A, Injunctive Relief –** ***Praxair shall operate the Facility in accordance with the ADEQ approved Operations and Maintenance Plan.*** The citation factual description explained that excessive emissions were reported to ADEQ by Praxair on 2/27/06, 3/15-16/06, 5/22/06, 8/12/06, 8/21/06, 9/6/06, and 9/22/06. The events appear to be violations of the Consent Judgment's Operation and Maintenance Plan. The Consent Judgment stipulated key process parameter monitoring and maintenance activities which should have prevented excess emission by indicating problems with equipment, flow velocities, pressure changes with control devices, and/or other process issues. The compliance conditions for the above violation included providing all daily, monthly, quarterly and annual key process maintenance logs, records, etc. as stipulated in the Consent Judgment for the Guardians, Baghouses, Dynawaves, Ventilation Emergency Scrubber, and the Vertex Monitor. The facility's deadline to achieve compliance was on February 11, 2007 and was achieved on January 31, 2007.

4. Non-compliance with **Permit No. 23262**, **Attachment "A," Condition II-Emission Limits –** ***Permittee shall not emit in excess of the following compounds: arsenic Compounds, including arsine (0.222 grams/hour), phosphine (0.093 grams/hour), diborane (0.068 grams/hour), dichlorosilane (42.24 grams/hour), silane (2.807), and diethyltelluride (0.0002 grams/hour).*** The citation factual description explained that excessive emissions were reported to ADEQ by Praxair on 4/7/06, 5/15/06, 7/12/06, 7/26/06, 8/15/06, 8/24/06, 8/27/06, 9/6/06, and 9/14/06. The excessive emissions included arsine and diborane. ADEQ received requested documentation from Praxair, and determined on March 19, 2007, that the facility had achieved compliance.

VII. PREVIOUS PERMITS

Table 3, below, lists the previous permits issued to this facility

Table 3 – Previous permits

Permit Number	Issuance Date	Explanation
65024	July 27, 1989	Installation Permit
1001267	August 31, 2000	Minor Revision to add ammonia handling operations
1001644	October 29, 2001	Minor Revision to expand arsine production capacity

VIII. AMBIENT AIR IMPACT ANALYSIS

A. Praxair conducted an Ambient Air Impact Analysis to demonstrate protection of the Arizona Ambient Air Quality Guidelines (AAAQGs). ADEQ reviewed this analysis and determined that the modeling approach is acceptable and that the estimated impacts associated with the permitted emission rates are not anticipated to result in adverse impacts to public health. Emission limits are included in the permit for arsine to ensure the facility's operation as a

synthetic minor source of HAPs and also to ensure that predicted concentrations of all pollutants in the ambient air will not exceed the corresponding AAAQG. With these limits, the predicted maximum concentrations are not expected to exceed the AAAQG thresholds. Table 4, below, compares the maximum predicted impacts of arsine to the AAAQG thresholds.

Table 4 – Comparison of modeled impacts to AAAQGs

Pollutant	Maximum Predicted Concentration ($\mu g/m^3$)	AAAQG threshold ($\mu g/m^3$)
1-hr impact	0.28	0.28
24-hr impact	0.066	0.073
Annual impact	1.8×10^{-4}	2.0×10^{-4}